Qualms Regarding the Range of Validity of the Glansdorff–Prigogine Criterion for Stability of Non-Equilibrium States

(thermodynamics/entropy/chemical reactions)

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ABSTRACT   Doubt is raised concerning the range of validity of a stability criterion for non-equilibrium states which has been proposed by Glansdorff and Prigogine. In the case of a particular autocatalytic reaction, the stability analysis presented by Glansdorff and Prigogine, and by Eigen and by Katchalsky in their reviews of this problem, does not agree with our analysis, which is based upon exact solution of the relevant rate equations. We also find disagreement between the analysis based upon the Glansdorff–Prigogine criterion and our analysis of a second example which involves non-equilibrium steady states. The situation is quite delicate because seemingly innocent approximations (e.g., the use of specialized conditions in the autocatalytic reaction $X + Y \rightleftarrows 2X$ discussed in the sequel) may lead to the impression that the scope of validity of the criterion is wider than it actually is. By considering the stability of the equilibrium state, we conclude that the second differential of the entropy, which is at the heart of the Glansdorff–Prigogine criterion, is likely to be relevant for stability questions close to equilibrium only.

During the last decade Prigogine and coworkers have been attempting to develop a theory for non-equilibrium thermodynamical phenomena which would be valid far from full equilibrium, and which would apply both to closed systems which asymptotically approach equilibrium, and to systems subject to inputs or constraints such that these systems developed, asymptotically in time, steady states. These efforts resulted in the publication of a book, *Thermodynamic Theory of Structure, Stability, and Fluctuations* (1), which presented the accomplishments as of 1971. At about the same time, Eigen (2) presented a theory for biomolecular evolution which stressed the importance of the theory developed by Prigogine, Katchalsky (3) wrote an essay which reviewed its essential points in the case of chemical rections, and Nicolis (4) wrote a critical review article for the entire subject.

Certain explicit and implicit claims regarding this theory (1–5) have led us to assess its range of validity and it is our purpose in this paper to present some of our considerations. We do so by examining the stability properties of a particular autocatalytic chemical reaction which has been discussed as an example by Prigogine (1), Eigen (2), and Katchalsky (3). When the Glansdorff–Prigogine criterion for stability is applied to this example, it is found that there is a region of instability far from full equilibrium. The autocatalytic nature of the reaction is offered as the basis for the instability. We find that the rate equations for this example may be solved exactly for all values of the concentration variables, and that the exact solution exhibits stability throughout a region whose stability cannot be determined by the Glansdorff–Prigogine

criterion. When another example, of the type considered by Glansdorff, Prigogine, and Nicolis (1, 4), is examined we find a regime of stable steady states on the basis of "normal mode" analysis, which their stability criterion, based upon the so-called excess entropy production, cannot demonstrate is stable. These results strongly emphasize that the Glansdorff–Prigogine criterion for stability is at best only a *sufficient condition* for stability, a fact recognized, but not sufficiently stressed by Glansdorff and Prigogine, and so the violation of this criterion *does not necessarily* imply the lack of stability. We believe that a stability criterion based upon the second differential of the entropy provides a useful condition only in a neighborhood of full equilibrium, and it does so because of its initimate connection with the second law of thermodynamics. For general non-equilibrium states, the examples treated in this paper show that the time derivative of the second differential of the entropy may be either positive or negative, and that a negative sign does not imply instability. These points will be detailed in the following sections.

Autocatalytic reaction example

In this section we present the details of the particular autocatalytic reaction which has been used as an example for the Glansdorff–Prigogine stability criterion. The reaction is an autocatalytic isomerization

$$X + Y \underset{k'}{\overset{k}{\rightleftarrows}} 2X$$
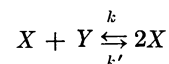
It is presumed that the reaction proceeds at constant temperature and pressure, and it is, therefore, governed by the Gibbs free energy. Since there is no external flow of molecules, the total number of molecules is constant. Therefore, if the number of molecules of types X and Y are denoted by α and β respectively, then $\alpha + \beta = C$ where C is constant. The rate of reaction, J, is defined by $J \equiv d\alpha/dt$ and is given by

$$J = k\alpha\beta - k'\alpha^2 \qquad [1]$$

This may be reexpressed as

$$d\alpha/dt = (k + k')\alpha(\alpha^* - \alpha) \qquad [2]$$

where $\alpha^* \equiv kC/(k + k')$. The rate, $d\alpha/dt$, is a quadratic function of α and is shown diagrammatically in Fig. 1. The equilibrium value is clearly α^*, and $\alpha = 0$ corresponds with a metastable steady state which we shall not consider further.

The affinity for this reaction is defined by

$$A(\alpha) = K_B T \ln(K/Q) \qquad [3]$$

where K_B is Boltzmann's constant, T is the absolute temperature, $K \equiv k/k'$ and $Q \equiv \alpha/\beta$. Since the differential of the Gibbs free energy, G, is related to the affinity by $dG = -Ad\alpha$ (6), one obtains

$$dG/dt = -AJ \qquad [4]$$
$$= -k'\alpha^2 K_B T[(K/Q) - 1] \ln (K/Q)$$
$$\leq 0$$

The final inequality follows from the fact that $(x - 1)$ and $\ln x$ always have the same sign, and equality occurs when $(K/Q) = 1$, which is the condition for equilibrium. Eq. [4] represents the second law of thermodynamics for this reaction. We have used a free energy, G, which as a function of α has the same form for non-equilibrium states as it does in equilibrium. This is in keeping with the spirit of the assumption of local equilibrium which is made throughout discussions of these problems (1, 4).

The Glansdorff-Prigogine Criterion

The reaction just described is said to be stable in the sense of Liapunov (7) if given any $\epsilon > 0$ there exists $\delta > 0$ such that whenever $|\alpha(0) - \alpha^*| < \delta$ then $|\alpha(t) - \alpha^*| < \epsilon$ for all $t > 0$. This may be generalized somewhat by expressing stability with: given any $\epsilon > 0$ there exists $\delta > 0$ such that whenever $|\alpha_1(0) - \alpha_2(0)| < \delta$ then $|\alpha_1(t) - \alpha_2(t)| < \epsilon$ for all $t > 0$ (7).

A Liapunov function for this reaction is any function of α, $L(\alpha)$, such that $L(\alpha)$ is negative semi-definite and $d[L(\alpha)]/dt$ is positive semi-definite. If a Liapunov function, $L(\alpha)$, exists for this reaction, then a theorem states that the reaction is stable in the sense of Liapunov (7). The Glansdorff-Prigogine criterion for stability is based upon exhibiting a Liapunov function for the reaction.

Glansdorff and Prigogine argue for the existence of a general, universal Liapunov function suitable for analysis of arbitrary reactions. We briefly outline the construction of this Liapunov function for chemical reactions of the type being considered. Let the free energy, G, be a function of temperature, T, pressure, P, and the numbers of molecules of types i, N_i. Therefore, the variation of G around its value at T°, P°, and N_i°, up to second order is

$$G = G^\circ + \delta G + \tfrac{1}{2}\delta^2 G \qquad [5]$$

where G° is the value of G at T°, P°, and N_i°, and

$$\delta G = -S\delta T + V\delta P + \sum_i \mu_i \, \delta N_i \qquad [6]$$

wherein the entropy $S \equiv -\left(\dfrac{\partial G}{\partial T}\right)_{P^\circ N_i^\circ}$, the volume $V \equiv \left(\dfrac{\partial G}{\partial P}\right)_{T^\circ,N_i^\circ}$ and the chemical potentials $\mu_i \equiv \left(\dfrac{\partial G}{\partial N_i}\right)_{T^\circ P^\circ N_i^\circ \neq i}$, and

$$\delta^2 G = \delta S \delta T + \delta V \delta P + \sum_{ij}\left(\frac{\partial \mu_i}{\partial N_j}\right)_0 \delta N_i \delta N_j + \sum_i \left(\frac{\partial \mu_i}{\partial T}\right)_0$$
$$\times \delta T \delta N_i + \sum_i \left(\frac{\partial \mu_i}{\partial P}\right)_0 \delta P \delta N_i \quad [7]$$

which follows from Eq [6] because $\delta^2 T = \delta^2 P = \delta^2 N_i = 0$ since these are the independent variables. Clearly, at constant
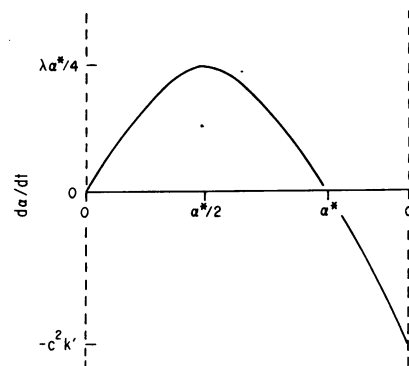

Fig. 1.   The rate of the autocatalytic reaction $X + Y \rightleftarrows 2X$ as a function of α, the concentration of X. α varies between 0 and c and has the equilibrium value α^*.

temperature and pressure we get

$$\delta^2 G = \sum_{ij}\left(\frac{\partial \mu_i}{\partial N_j}\right)_0 \delta N_i \delta N_j \qquad [8]$$

Using the Gibbs relation for the total differential of the entropy, S, as a function of the independent variables, E, V, and N_i

$$T\delta S = \delta E + P\delta V - \sum_i \mu_i \delta N_i \qquad [9]$$

leads to (8)

$$\delta^2 S = \delta T^{-1}\delta E + \delta\,(P/T)\delta V - \sum_i \delta\left(\frac{\mu_i}{T}\right)\delta N_i \qquad [10]$$

which at constant temperature and pressure becomes

$$\delta^2 S = -\frac{1}{T^\circ}\sum_{ij}\left(\frac{\partial \mu_i}{\partial N_j}\right)_0 \delta N_i \delta N_j \qquad [11]$$

Comparing [8] and [11] shows that $-T^\circ\delta^2 S = \delta^2 G$. Consequently, in the following we shall be concerned with the second differential of the entropy, $\delta^2 S$, rather than with the second differential of the free energy, $\delta^2 G$. The definition of the chemical potential, $\mu_i \equiv (\partial G/\partial N_i)$ and the assumption of local equilibrium which justifies using these expressions to describe non-equilibrium states imply that $\partial \mu_i/\partial N_j = \partial^2 G/\partial N_i \partial N_j$, is symmetric in i and j and is positive as is the case near full equilibrium.

Consequently, Eq. [11] implies that $\delta^2 S$ is negative semi-definite not only close to full equilibrium, but in general, and it is this observation that is of unquestioned novelty. Returning to Eqs. [4] and [5], it is seen that close to full equilibrium where $\delta G = 0$ that

$$\frac{d}{dt}\delta^2 G = -T^\circ \frac{d}{dt}\delta^2 S \leq 0. \qquad [12]$$

Therefore, at least close to full equilibrium $d(\delta^2 S)/dt \geq 0$ and $\delta^2 S$ may serve as a Liapunov function. Glansdorff and Prigogine suggest that because $\delta^2 S$ is negative semi-definite even far from full equilibrium, then perhaps it is a Liapunov function everywhere (9).

Before we apply the Glansdorff-Prigogine criterion to the autocatalytic reaction described earlier, it is necessary to re-express Eq. [12] in still another form. This new form introduces the reaction rates and affinities into the stability cri-
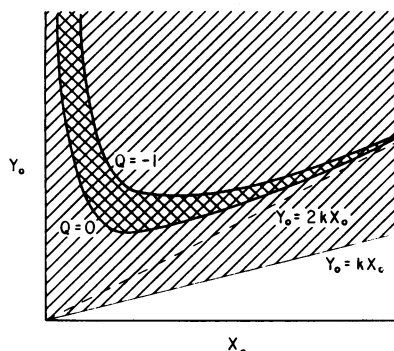
Fig. 2. The hatched area gives the regime of steady states for the reaction scheme discussed in the text. The cross-hatching indicates the region for which $-1 < Q < 0$

terion. Suppose that the molecules given by N_i engage in reactions ρ with rates J_ρ and stoichiometric coefficients $\nu_{i\rho}$ (10). The rate equations are then

$$\frac{d}{dt} N_i = \sum_\rho \nu_{i\rho} J_\rho \qquad [13]$$

The affinities are defined by ref. 10

$$A_\rho \equiv - \sum_i \nu_{i\rho} \mu_i \qquad [14]$$

where μ_i is the chemical potential for molecular species i. Therefore, returning to Eq. [11], and using Eqs. [13] and [14] gives

$$\frac{d}{dt} \delta^2 S = - \frac{1}{T^\circ} \sum_{ij} \frac{d}{dt} \left[\left(\frac{\partial \mu_i}{\partial N_j}\right)_0 \delta N_i \delta N_j \right] \qquad [15]$$

$$= - \frac{1}{T^\circ} \sum_{ij} 2 \left(\frac{\partial \mu_i}{\partial N_j}\right)_0 \delta N_j \frac{d}{dt} \delta N_i$$

$$= - \frac{2}{T^\circ} \sum_i \delta \mu_i \frac{d}{dt} \delta N_i$$

$$= - \frac{2}{T^\circ} \sum_i \sum_\rho \delta \mu_i \nu_{i\rho} \delta J_\rho$$

$$= \frac{2}{T^\circ} \sum_\rho \delta A_\rho \delta J_\rho$$

In Eq. [15] the second equality involves the symmetry of $\partial \mu_i/\partial N_j$ with respect to i and j, and $d/dt\ (\partial \mu_i/\partial N_j)_0 = 0$. The third equality uses $\delta \mu_i \equiv \sum_j (\partial \mu_i/\partial N_j)_0 \delta N_j$, the fourth uses Eq. [13], and the last equality uses Eq. [14]. Therefore, the stability criterion can be expressed as

$$\sum_\rho \delta J_\rho \delta A_\rho > 0. \qquad [16]$$

Glansdorff and Prigogine suggest, and Eigen asserts, that a violation of inequality [16] is closely related to instability (11, 12).

In the case of the autocatalytic reaction Eqs. [1] and [3] provide for δA and δJ

$$\delta A = - K_B TC \frac{1}{\alpha(C - \alpha)} \delta \alpha \qquad [17]$$

$$\delta J = (k + k')\ (\alpha^* - 2\alpha)\ \delta \alpha$$

Now, in the far from full equilibrium regime given by $\alpha < \alpha^*/2$ it is clear from Eq. [17] that $\delta A \delta J < 0$! Therefore, it has been asserted that in this regime the reaction shows instability (11–13). If it were so that $\delta A \delta J < 0$ remained true for all future times, then instability would indeed be implied by the First Instability Theorem of Liapunov (14). However, in all three of the references given this persistence of $\delta A \delta J < 0$ is achieved by entirely neglecting the reverse reaction throughout all future time by taking $k' = 0$ and by fixing the concentration of Y so that no steady states can occur. In the next section we shall expand on this point further.

Exact treatment of the autocatalytic reaction

Eq. [2] admits of an exact solution if one uses the elementary techniques of separation of variables and the method of partial fractions. The solution of Eq. [2], as may be seen by substitution, is

$$\frac{\alpha(t)}{\alpha^*} = \left[1 - [\exp(-\lambda t)]\left[1 - \frac{\alpha^*}{\alpha(0)} \right] \right]^{-1} \qquad [18]$$

where $\alpha(0)$ is the initial value, and $\lambda \equiv (k + k')\alpha^* = kC$. For $\alpha(0) < \alpha^*$ the solution monotonically approaches α^* from below, whereas for $\alpha(0) > \alpha^*$ the solution monotonically approaches α^* from above. If we return to the Liapunov characterizations of stability (7, 9), we see that for stability we meet the required condition because Eq. [18] gives monotone behavior. Moreover, from Eq. [18] it follows that

$$\frac{|\alpha_1(t) - \alpha_2(t)|}{\alpha^*} = \frac{|\alpha_1(0) - \alpha_2(0)|\alpha_1(t)\alpha_2(t)}{\alpha_1(0)\alpha_2(0)} \exp(-\lambda t) \qquad [19]$$

Therefore, in the interval $[a, C]$ where $a > 0$ we have

$$\frac{|\alpha_1(t) - \alpha_2(t)|}{\alpha^*} \leq \frac{|\alpha_1(0) - \alpha_2(0)|C^2}{a^2} \exp(-\lambda t) \qquad [20]$$

Inequality [20] implies that given $\epsilon > 0$, then if $\delta = a^2\epsilon/C^2\alpha^*$, then $|\alpha_1(0) - \alpha_2(0)| < \delta$ implies that $|\alpha_1(t) - \alpha_2(t)| < \epsilon \exp(-\lambda t) \leq \epsilon$ for all $t > 0$. This is clearly valid even for $a < \alpha < \alpha^*/2$! In this regime it is true that if $a < \alpha_1(0) < \alpha_2(0) < \alpha^*/2$, then, as can be seen in Fig. 1, $\alpha_2(t)$ initially moves away from $\alpha_1(t)$ until they reach the $\alpha^*/2$ point where they begin to close together again as their rates decrease. However, this initial separating motion is not instability since it may be properly bounded as shown here, above. Moreover, as soon as $\alpha(t)$ reaches $\alpha^*/2$ then δJ changes sign and $\delta A \delta J > 0$ is true for all future times. This is obscured by the reaction conditions used by Prigogine, Eigen, and Katchalsky (11–13). The separating motion for $a < \alpha < \alpha^*/2$ is a result of the autocatalytic nature of the reaction, and even though it does not imply instability in the sense of Liapunov, as we have shown, it is nevertheless qualitatively different behavior than for $\alpha^*/2 < \alpha < C$. Katchalsky has stressed this point, and it is reflected in the change of sign in $\delta J \delta A$, but Liapunov-stability is not violated.

The Liapunov-stability conditions are known to be sufficient conditions (15, 16), and while this point appears in Glansdorff and Prigogine's theory, it is not in our opinion sufficiently stressed to prevent inadvertent misapplication.

A steady state example

So far we have only treated the far from full equilibrium behavior of a reaction which ultimately goes to equilibrium. In this section we shall treat another reaction model of the

type considered by Glansdorff and Prigogine (17). The reaction are

[a] $A \rightleftarrows X$

[b] $Y + 2X \rightleftarrows 3X$

[c] $B + X \rightleftarrows Y + D$

[d] $X \rightleftarrows E$

The rate constants for the forward reactions are all unity and the reverse reactions all have rate constants equal to k. Nonequilibrium steady states are achieved by fixing the concentrations of A, B, C and E, and it is presumed for convenience that $E = A/k^2$. We shall denote the number of molecules of types A, B, D, E, X, and Y by A, B, D, E, X and Y respectively. The steady state values of X and Y, to be denoted by X_0 and Y_0, are given by Eq. [17]

$$X_0 = A/k \text{ and } Y_0 = X_0(kX_0^2 + B)/(X_0^2 + kD) \quad [21]$$

Normal mode analysis is performed by linearizing the rate equations around the steady state values for X and Y, followed by determination of the eigenvalues of the resulting 2×2 coupling matrix. The eigenvalue equation is

$$\omega^2 + [X_0^2 + B + 1 - 2X_0Y_0 + k(3X_0^2 + D + 1)]\omega$$
$$+ (1 + k)(X_0^2 + kD) = 0 \quad [22]$$

Stability, according to normal mode analysis, requires that the real parts of the solutions to Eq. [22] be negative. If the real part of either root is positive, then the steady state is not stable.

The Glansdorff-Prigogine criterion for stability requires that we look at $d\delta^2S/dt = (2/T) \sum_i \delta J_i \delta A_i$. The reaction rates and affinities for the reactions [a], [b], [c], and [d] are

$$J_a = A - kX \qquad A_a = K_BT \ln (A/kX) \qquad [23]$$

$$J_b = X^2Y - kX^3 \qquad A_b = K_BT \ln (Y/kX)$$

$$J_c = BX - kYD \qquad A_c = K_BT \ln (BX/kYD)$$

$$J_d = X - kE \qquad A_d = K_BT \ln (X/kE)$$

Eqs. [23] lead to

$$\frac{d}{dt} \delta^2S = \frac{2}{T} \sum_i \delta J_i \delta A_i$$

$$= K_B [(k + 1 + B + 3kX_0^2 - 2X_0Y_0)/X_0](\delta X)^2$$

$$+ K_B [(Y_0X_0^2 - BX_0 - kDY_0 - 3KX_0^3)/Y_0X_0]$$

$$\times (\delta X)(\delta Y) + K_B [(X_0^2 + kD)/Y_0](\delta Y)^2 \quad [24]$$

This expression is not positive semi-definite for all possible steady states because the $(\delta X)^2$ coefficient may sometimes be negative. We shall proceed to show that there are steady states for which the coefficient of $(\delta X)^2$ is negative, but for which the corresponding solutions to Eq. [22] have negative real parts.

In order to simplify the algebra we consider the special case of $D = 0$. The steady state Eqs. [21] become

$$X_0 = A/k \text{ and } Y_0 = A + Bk/A \quad [25]$$

This implies that X_0 can have any positive value and that for a given value of X_0, Y_0 can have any value greater than kX_0. Therefore, the manifold of possible steady states is the set of

all points on or above the $Y_0 = kX_0$ line in the $X_0 - Y_0$ plane as shown in Fig. 2. We partially delineate the subregion of steady states for which $d(\delta^2S)/dt$ contains a negative coefficient for $(\delta X)^2$. Eq [24] shows this subregion to be determined by

$$k + 1 + B + 3kX_0^2 - 2X_0Y_0 < 0 \quad [26]$$

which in conjunction with Eq. [25] becomes

$$Q \equiv k + 1 + 2kX_0^2 - Y_0X_0 < 0 \quad [27]$$

For a given value of X_0 all values of Y_0 which are greater than $2kX_0 + (k + 1)/X_0$ will satisfy Eq. [27]. This region is entirely within the set of possible steady states and the region for which Q falls between zero and minus one is shown by the cross-hatching in Fig. 2. Thus, within this special subregion $d(\delta^2S)/dt$ is an indefinite form which can be negative. Glansdorff and Prigogine would suggest that this could be a threat to stability. However, returning to Eq. [22], with $D = 0$, we find that the normal mode analysis leads to the eigenvalue equation

$$\omega^2 + [X_0^2 + Q]\omega + (1 + k)X_0^2 = 0 \quad [28]$$

Therefore, in the region where $-1 \leq Q \leq 0$, if $X_0 > 1$, then the roots to Eq. [28] have negative real parts, which implies stability. Consequently, we find the Glansdorff-Prigogine stability criterion to be of no value for these steady states. In particular it seems to us not justified to consider $\delta A \delta J$ to be a Liapunov function or and to use it to determine the limits of stability.

Concluding remarks

We feel that the qualms presented here deserve consideration because of the intricacy and delicacy of the problem of stability. In our presentation of the derivation of the Glansdorff-Prigogine stability criterion we have indicated why it is plausible that this criterion may only apply close to full equilibrium where the second law of thermodynamics, as represented by Eq. [4], implies that δ^2S is indeed a Liapunov function. Near steady states which are far from equilibrium, there is no guarantee that $d(\delta^2S)/dt$ will behave appropriately. Indeed, our examples show that it does not and that extreme caution is indicated. We feel that this reflects the fact that stability far from equilibrium requires kinetic, in addition to purely thermodynamic, considerations.

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